

1 **STABILIZED PHENOLIC RESOLE RESIN COMPOSITIONS**
2 **AND THEIR USE**

3
4 **Technical Field of the Invention**

5 This invention relates to a stabilized phenolic resole resin composition comprising a
6 phenolic resole resin and an effective stabilizing amount of an ortho ester. The invention
7 also relates to phenolic urethane binders prepared with the phenolic resole resin
8 compositions, and the use of the binders to make foundry mixes, foundry shapes, and
9 metal castings.

10

11 **Background of the Invention**

12 One of the major processes used in the foundry industry for making metal parts is sand
13 casting. In sand casting, disposable foundry shapes (usually characterized as molds and
14 cores) are made by shaping and curing a foundry binder system that is a mixture of sand
15 and an organic or inorganic binder. The binder is used to strengthen the molds and
16 cores.

17

18 Two of the major processes used in sand casting for making molds and cores are the no-
19 bake process and the cold-box process. In the no-bake process, a liquid curing agent is
20 mixed with an aggregate and shaped to produce a cured mold and/or core. In the cold-
21 box process, a gaseous curing agent is passed through a compacted shaped mix to
22 produce a cured mold and/or core. Phenolic urethane binder, cured with a gaseous
23 tertiary amine catalyst, are often used in the cold-box process to hold shaped foundry
24 aggregate together as a mold or core. See for example U.S. Patent 3,409,579. The
25 phenolic urethane binder system usually consists of a phenolic resin component and
26 polyisocyanate component, which are mixed with sand prior to compacting and curing
27 to form a foundry binder system.

28

29 Among other things, the binder must have a low viscosity, be gel-free, remain stable
30 under use conditions, and cure efficiently. The foundry binder system made by mixing
31 sand with the binder must have adequate benchlife or the mix will not shape and cure

1 properly. The cores and molds made with the binders must have adequate tensile
2 strengths under normal and humid conditions, and release effectively from the pattern.
3 Binders that meet all of these requirements are not easy to develop.

4

5 One of the problems with the phenolic resole resins used in phenolic urethane binders is
6 that they are heat sensitive, and thus are not stable when stored at or exposed to elevated
7 temperature for a prolonged period of time. This causes the viscosity of the resin to
8 increase, or in extreme cases, the resin will gel. This seriously adversely affects the
9 quality and performance of the binder.

10

11 Ortho esters are known in the prior art to stabilize organic isocyanates. U. S. Patent
12 3,535,359 (Chadwick) discloses that certain ortho-esters are capable of stabilizing a
13 polyisocyanate against several different kinds of degradation, for instance moisture, and
14 viscosity increases, even when only small amounts of ortho esters are used. The
15 stabilized isocyanates are useful in the preparation of polyurethane foam, nonporous
16 plastics including polyurethane castings such as gear wheels and the like, and coating
17 compositions. Chadwick does not disclose the use of such polyisocyanates in foundry
18 binders, foundry mixes, or the preparation of foundry shapes and metal castings.

19

20 U.S. Patent 6,288,139 discloses phenolic urethane binders wherein the polyisocyanate
21 component contains an ortho ester. The patent indicates that, when added to a
22 polyisocyanate component that contains a non reactive organic solvent, the ortho ester
23 improves the tensile strength of foundry shapes. It also indicates that polyisocyanate
24 components containing the ortho ester have lower turbidity, which indicates that it is
25 more stable or homogeneous. As a result the polyisocyanate component will not be
26 subjected to settling of particulate matter, and will be easier to pump. This patent does
27 not teach or suggest the use of ortho esters in the phenolic resole resin component of the
28 phenolic urethane binder.

29

1 **Summary of the Invention**

2 This invention relates to stabilized phenolic resole resin compositions comprising a
3 phenolic resole resin and an effective stabilizing amount of an ortho ester. The invention
4 also relates to phenolic urethane binders prepared with the phenolic resole resin
5 compositions, and the use of the binders to make foundry mixes, foundry shapes, and
6 metal castings.

7
8 The addition of the ortho ester was found to be an effective stabilizing agent to improve
9 the shelf stability of the phenolic resole resin composition. The advantages of using the
10 ortho ester in the phenolic resole resin composition are:

11

12 (1) the phenolic resole resin composition ~~better has~~ has better shelf storage
13 stability if it contains the ortho ester, and

14

15 (2) the phenolic resole resin composition has improved heat stability at
16 elevated temperatures if it contains the ortho ester.

17

18 Shelf stability and heat stability are demonstrated because the phenolic resole resin
19 composition does not undergo viscosity increase or gelation, even when subjected to
20 increased temperatures. This advantage is particular important when the phenolic resole
21 resin composition is stored and exposed at elevated temperatures during summer time.

22

23 **Detailed Description of the Invention**

24 The phenolic resole resin used in the phenolic resole resin composition is preferably
25 prepared by reacting an excess of aldehyde with a phenol in the presence of either an
26 alkaline catalyst or a metal catalyst. The phenolic resins are preferably substantially free
27 of water and are organic solvent soluble. The preferred phenolic resins used in the
28 subject binder compositions are well known in the art, and are specifically described in
29 U.S. Patent 3,485,797, which is hereby incorporated by reference. These resins, known
30 as benzylic ether phenolic resole resins, are the reaction products of an aldehyde with a

1 phenol. They contain a preponderance of bridges joining the phenolic nuclei of the
2 polymer, which are ortho-ortho benzylic ether bridges. They are prepared by reacting an
3 aldehyde and a phenol in a mole ratio of aldehyde to phenol of at least 1:1 in the
4 presence of a metal ion catalyst, preferably a divalent metal ion such as zinc, lead,
5 manganese, copper, tin, magnesium, cobalt, calcium, and barium.

6

7 Alkoxy-modified benzylic ether phenolic resole resins can also be used. The resins are
8 prepared by reacting an excess of aldehyde with a phenol and an alcohol in the presence of
9 a metal ion catalyst according to methods well known in the art. Alternatively, they can be
10 prepared by preparing a benzylic ether phenolic resole resin and post-capping with the
11 alcohol. See, for example, U.S. Patent 4,546,124 for a discussion of how these resins are
12 prepared.

13

14 The phenols use to prepare the phenolic resole resins include any one or more of the
15 phenols which have heretofore been employed in the formation of phenolic resins and
16 which are not substituted at either the two ortho-positions or at one ortho-position and
17 the para-position. These unsubstituted positions are necessary for the polymerization
18 reaction. Any of the remaining carbon atoms of the phenol ring can be substituted. The
19 nature of the substituent can vary widely and it is only necessary that the substituent not
20 interfere in the polymerization of the aldehyde with the phenol at the ortho-position
21 and/or para-position. Substituted phenols employed in the formation of the phenolic
22 resins include alkyl-substituted phenols, aryl-substituted phenols, cyclo-alkyl-
23 substituted phenols, aryloxy-substituted phenols, and halogen-substituted phenols, the
24 foregoing substituents containing from 1 to 26 carbon atoms and preferably from 1 to 12
25 carbon atoms.

26

27 Specific examples of suitable phenols include phenol, 2,6-xylenol, o-cresol, p-cresol,
28 3,5-xylenol, 3,4-xylenol, 2,3,4-trimethyl phenol, 3-ethyl phenol, 3,5-diethyl phenol, p-
29 butyl phenol, 3,5-dibutyl phenol, p-amyl phenol, p-cyclohexyl phenol, p-octyl phenol,

1 3,5-dicyclohexyl phenol, p-phenyl phenol, p-crotyl phenol, 3,5-dimethoxy phenol, 3,4,5-
2 trimethoxy phenol, p-ethoxy phenol, p-butoxy phenol, 3-methyl-4-methoxy phenol, and
3 p-phenoxy phenol. Multiple ring phenols such as bisphenol A and bisphenol F are also
4 suitable.

5

6 The aldehyde used to react with the phenol has the formula RCHO wherein R is a
7 hydrogen or hydrocarbon radical of 1 to 8 carbon atoms. The aldehydes reacted with the
8 phenol can include any of the aldehydes heretofore employed in the formation of
9 phenolic resins such as formaldehyde, acetaldehyde, propionaldehyde, furfuraldehyde,
10 and benzaldehyde. The most preferred aldehyde is formaldehyde.

11

12 The phenolic resin used must be liquid or organic solvent-soluble. The phenolic resin
13 composition generally contains an organic solvent. The amount of solvent used should
14 be sufficient to result in a binder composition permitting uniform coating thereof on the
15 aggregate and uniform reaction of the mixture. The specific solvent concentration for
16 the phenolic resin composition will vary depending on the type of phenolic resin
17 employed and its molecular weight. In general, the solvent concentration will be in the
18 range of up to 80% by weight of the resin solution and preferably in the range of 20% to
19 80%.

20

21 As was mentioned previously, the phenolic resole resin composition contains an ortho
22 ester. The ortho esters used have the formula R'C(OR)₃, where R' is hydrogen, alkyl,
23 alkenyl, aryl, haloalkyl and R is alky or alkenyl of 1 to 18 carbon atoms, chloroethyl, or
24 phenyl. The ortho esters are disclosed in U.S. Patent 3,535,359, which is incorporated
25 by reference into this specification. Preferably used are triethyl orthoformate, trimethyl
26 orthoformate, and mixtures thereof. The amount of ortho ester used is from 0.1 to 5.0
27 weight percent based upon the weight of the phenolic resole resin, preferably from 0.1
28 to 1.5 weight percent, most preferably from 0.1 to 0.4 weight percent

1 The phenolic resole resin compositions are used in the phenolic urethane binders. These
2 binders contain a phenolic resin component and a polyisocyanate component, and are
3 typically cured with a tertiary amine curing catalyst.

4

5 The polyisocyanate component of the binder typically comprises a polyisocyanate and
6 organic solvent. The polyisocyanate has a functionality of two or more, preferably 2 to
7 5. It may be aliphatic, cycloaliphatic, aromatic, or a hybrid polyisocyanate. Mixtures of
8 such polyisocyanates may be used. Also, it is contemplated that capped
9 polyisocyanates, prepolymers of polyisocyanates, and quasi prepolymers of
10 polyisocyanates can be used. Optional ingredients such as release agents may also be
11 used in the polyisocyanate hardener component.

12

13 Representative examples of polyisocyanates which can be used are aliphatic
14 polyisocyanates such as hexamethylene diisocyanate, alicyclic polyisocyanates such as
15 4,4'-dicyclohexylmethane diisocyanate, and aromatic polyisocyanates such as 2,4-, 2,4-,
16 2,6-toluene diisocyanate and 2,2'-, 2,4'-, 4,4'-diphenylmethane diisocyanate, and
17 dimethyl derivates thereof. Other examples of suitable polyisocyanates are 1,5-
18 naphthalene diisocyanate, triphenylmethane triisocyanate, xylylene diisocyanate, and the
19 methyl derivates thereof, polymethylenepolyphenyl isocyanates, chlorophenylene-2,4-
20 diisocyanate, and the like.

21

22 The polyisocyanates are used in sufficient concentrations to cause the curing of the
23 phenolic resin in the presence of the curing catalyst. In general the polyisocyanate ratio
24 of the polyisocyanate to the hydroxyl of the phenolic resin is from 1.25:1 to 1:1.25,
25 preferably about 1:1. Expressed as weight percent, the amount of polyisocyanate used is
26 from 10 to 500 weight percent, preferably 20 to 300 weight percent, based on the weight
27 of the phenolic resin.

28

1 The polyisocyanate is used in a liquid form. Solid or viscous polyisocyanate must be
2 used in the form of organic solvent solutions. In general, the solvent concentration will
3 be in the range of up to 80% by weight of the resin solution and preferably in the range
4 of 20% to 80%.

5

6 Those skilled in the art will know how to select specific solvents for the phenolic resin
7 component, and in particular the solvents required in the polyisocyanate component. It
8 is known that the difference in the polarity between the polyisocyanate and the phenolic
9 resins restricts the choice of solvents in which both components are compatible. Such
10 compatibility is necessary to achieve complete reaction and curing of the binder
11 compositions of the present invention. Polar solvents of either the protic or aprotic type
12 are good solvents for the phenolic resin, but have limited compatibility with the
13 polyisocyanate. Aromatic solvents, although compatible with the polyisocyanate, are
14 less compatible with the phenolic results. It is, therefore, preferred to employ
15 combinations of solvents and particularly combinations of aromatic and polar solvents.

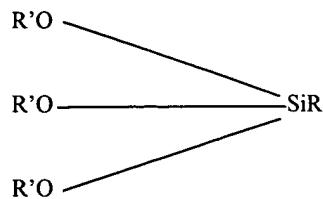
16

17 Examples of aromatic solvents include xylene and ethylbenzene. The aromatic solvents
18 are preferably a mixture of aromatic solvents that have a boiling point range of 125° C
19 to 250° C. The polar solvents should not be extremely polar such as to become
20 incompatible with the aromatic solvent. Suitable polar solvents are generally those
21 which have been classified in the art as coupling solvents and include furfural, furfuryl
22 alcohol, cellosolve acetate, butyl cellosolve, butyl carbitol, diacetone alcohol, and
23 "Texanol".

24

25 The binder may also contain a silane (typically added to the phenolic resin component)
26 having the following general formula:

27



1

2

3 wherein R' is a hydrocarbon radical and preferably an alkyl radical of 1 to 6 carbon
4 atoms and R is an alkyl radical, an alkoxy-substituted alkyl radical, or an alkyl-amine-
5 substituted alkyl radical in which the alkyl groups have from 1 to 6 carbon atoms. The
6 silane is preferably added to the phenolic resin component in amounts of 0.01 to 2
7 weight percent, preferably 0.1 to 0.5 weight percent based on the weight of the phenolic
8 resin component.

9

10 When preparing an ordinary sand-type foundry shape, the aggregate employed has a
11 particle size large enough to provide sufficient porosity in the foundry shape to permit
12 escape of volatiles from the shape during the casting operation. The term "ordinary
13 sand-type foundry shapes," as used herein, refers to foundry shapes which have
14 sufficient porosity to permit escape of volatiles from it during the casting operation.

15

16 The preferred aggregate employed for preparing ordinary foundry shapes is silica
17 wherein at least about 70 weight percent and preferably at least about 85 weight percent
18 of the sand is silica. Other suitable aggregate materials include zircon, olivine,
19 aluminosilicate, Remove Comma sand, chromite sand, and the like. Although the
20 aggregate employed is preferably dry, it can contain minor amounts of moisture.

21

22 In molding compositions, the aggregate constitutes the major constituent and the binder
23 constitutes a relatively minor amount. In ordinary sand type foundry applications, the
24 amount of binder is generally no greater than about 10% by weight and frequently
25 within the range of about 0.5% to about 7% by weight based upon the weight of the

1 aggregate. Most often, the binder content ranges from about 0.6% to about 5% by
2 weight based upon the weight of the aggregate in ordinary sand-type foundry shapes.

3

4 The binder compositions are preferably made available as a two-package system with
5 the phenolic resin component in one package and the polyisocyanate component in the
6 other package. Usually, the phenolic resin component is first mixed with sand and then
7 the polyisocyanate component is added. Methods of distributing the binder on the
8 aggregate particles are well known to those skilled in the art.

9

10 The foundry binder system is molded into the desired shape, such as a mold or core, and
11 cured. Curing by the cold-box process is carried out by passing a volatile tertiary amine,
12 preferably triethyl amine, through the shaped mix as described in U.S. Patent 3,409,579.
13 Curing by the no-bake process takes place by mixing a liquid amine curing catalyst into
14 the foundry binder system, shaping it, and allowing it to cure.

15

16 Useful liquid amines have a pK_b value generally in the range of about 7 to about 11.
17 Specific examples of such amines include 4-alkyl pyridines, isoquinoline, arylpyridines,
18 1-methylbenzimidazole, and 1,4-thiazine. Preferably used as the liquid tertiary amine
19 catalyst is an aliphatic tertiary amine, particularly tris (3-dimethylamino) propylamine.
20 In general, the concentration of the liquid amine catalyst will range from about 0.2 to
21 about 5.0 percent by weight of the phenolic resin, preferably 1.0 percent by weight to
22 4.0 percent by weight, most preferably 2.0 percent by weight to 3.5 percent by weight
23 based upon the weight of the phenolic resin.

24

25 EXAMPLES

26 While the invention has been described with reference to a preferred embodiment, those
27 skilled in the art will understand that various changes may be made and equivalents may
28 be substituted for elements thereof without departing from the scope of the invention.
29 In addition, many modifications may be made to adapt a particular situation or material

1 to the teachings of the invention without departing from the essential scope thereof.
2 Therefore, it is intended that the invention not be limited to the particular embodiment
3 disclosed as the best mode contemplated for carrying out this invention, but that the
4 invention will include all embodiments falling within the scope of the appended claims.
5 In this application, all amounts and percentages are by weight, unless otherwise
6 expressly indicated. The following abbreviations are used in the examples:

7

8 TMOF trimethyl ortho-formate.
9
10 PEP SET® 1670/2670 a phenolic urethane no-bake foundry binder,
11 manufactured by Ashland Specialty Chemical Company.
12 PEP SET 1670 is the phenolic component and comprises
13 about 50-60 weight percent PR, 20-30 weight percent
14 aromatic solvent, and 10-20 weight percent ester solvent.
15 PEP SET 2670 is the isocyanate component and
16 comprises about 60-80 weight percent isocyanate, and 30-
17 40 weight percent aromatic solvents.

18

19 PR a polybenzylic ether phenolic resin prepared with zinc
20 acetate dihydrate as the catalyst and modified with the
21 addition of 0.09 mole of methanol per mole of phenol
22 prepared along the lines described in the examples of U.S.
23 Patent 3,485,797.

24

25 Wedron 540 sand silica sand commonly used in the foundry industry.

26

27 RH relative humidity.

28

29 ST striptime is the time interval for a foundry mix to reach a
30 green hardness of 90.

31

1 WT worktime is the time interval for a foundry mix to reach a
2 green hardness of 60.

3

4

5
6 The following examples demonstrate the use of TMOF in phenolic urethane no-bake
7 foundry binder applications.

8

9

10

11 **Examples A, 1, and 2**
12 **(Heat stability tests of phenolic resins)**

13
14 In order to test the heat stability of the phenolic resin compositions with and without
15 TMOF, 200 grams of PEP SET 1670 binder were placed in 8-oz plastic bottles. The
16 samples were stored at 60°C for 80 days. The viscosity of the samples was measured
17 after 1 day and after 80 days by using Brookfield viscosity cone and plate viscosity
18 method. The results are summarized in Table I.

19

20

21

22 **Table I**
23 **(Effect of TMOF on the Heat Stability of Phenolic Component)**
24 **(Samples stored at 60°C for 80 days)**

26 Phenolic component	27 TMOF ¹	27 Viscosity (cp)	27
		Day 1	Day 80
29 Control A ²	0.0	165	> 1,000,000, partially gelled
30 Example 1	0.7	163	2,640
31 Example 2	1.4	162	862

32
33
34 Table I shows that the incorporation of TMOF as stabilizing agent at levels of 0.7 and
35 1.4% by weight into the phenolic component (PEP SET 1670) greatly improved the

¹Weight percent based upon the weight of the phenolic resin component.

²PEP SET® 1670 phenolic resin component.

1 shelf storage stability of the phenolic component at 60°C. The control sample (A)
2 gelled out, while Example 1 and 2 were pourable liquids after 80 days storage at 60°C.
3 Table I also indicates that the higher level of TMOF used, the greater the heat stability
4 of the phenolic resole resin component. This is particular important during the hot
5 summer time, where the temperature can reach 50°C during the shipping and handling
6 of the foundry binder.

Examples B, 3, and 4

(Effect of using TMOF on strength of cores made with binder)

9 Test cores were made with PEP SET® 1670/2670 using Wedron 540 sand at a binder
10 level of 1.2%, based upon the weight of the sand, a Part I/PartII mix ratio of 55/45 mix
11 ratio, and PEP SET 3502 catalyst (4-phenyl propyl pyridine in an aromatic solvent) in
12 an amount of about 3 weight percent based upon the Part I.

13

14 Tensile strengths of test dog bone shapes were measured according to the AFS standard
15 tensile strength test. Determining the tensile strengths of the dog bone test shapes
16 enables one to predict how the mixture of sand and binder will work in actual foundry
17 facilities. The dog bones were stored for 1.0 hour, 3 hours and 24 hours in a constant
18 temperature room at relative humidity of 50% and a temperature of 25°C before
19 measuring their tensile strengths. Unless otherwise specified, the tensile strengths were
20 also measured on dog bone specimens stored 24 hours at a relative humidity (RH) of
21 90%. The results of these tests are shown in Table II.

Table II
(Effect of TMOF on sand tensile performance)

4	Binder	TMOF level ³	WT/ST (min)	1 Hr ↔↔↔↔	3 Hrs [psi]	24 Hrs →→→ @	24 Hr 90% RH
5	Control B	0.0	3.0/4.0	152	166	200	70
6	Example 3	0.7	3.8/4.2	159	181	212	65
7	Example 4	1.4	3.5/4.2	136	192	185	63

The data indicate that addition of TMOF to the phenolic resole resin component has little effect on the sand tensile strength development. The data in Tables I and II indicate that adding TMOF into the phenolic resin component, while increasing the heat stability of the phenolic resin component, does not adversely effect the desired core-making properties.

Examples C, 5, and 6

(Heat stability tests of phenolic resins where zinc catalyst was removed)

20 The procedure of Examples A, 1, and 2 was followed, except the zinc catalyst used to
21 make the resin was removed from the resin. The results are summarized in Table III.

Table III
(Effect of TMOF on the Heat Stability of Phenolic Component)
(Samples stored at 60°C for 80 days)

Phenolic component	TMOF ⁴	Viscosity (cp)	
		Day 1	Day 80
Control C	0.0	75	595
Example 5	0.7	74	367
Example 6	1.4	73	319

35 The data in Table III indicate that the phenolic resole resin component without the zinc
 36 catalyst had a much lower viscosity to begin with. However, the effect of TMOF on
 37 the heat stability of the phenolic component is still evident. The addition of TMOF to

³Weight percent based upon the weight of the phenolic resin component.

1 the phenolic resin component improved the heat stability of the phenolic resin
2 component, which is shown by the data indicating that there was little change in
3 viscosity in the samples containing the TMOF.

4

5 **Examples D, 7, and 8**

6 **(Effect of using TMOF on strength of cores made with binder)**

7 Test cores using the procedure set forth in Examples B, 3, and 4, except the phenolic
8 resin of Examples C, 5, and 6, which had the zinc catalyst removed, was used as the
9 resin. The results of these tests are shown in Table IV.

10

11 **Table II**
12 **(Effect of TMOF on sand tensile performance)**

Binder	TMOF level ⁵	WT/ST (min)	1 Hr ↔↔↔↔	3 Hrs [psi]	24 Hrs →→→ @	24 Hr 90% RH
Control D	0.0	6.5/7.5	157	186	235	102
Example 7	0.7	7.0/8.3	133	183	253	104
Example 8	1.4	8.5/10.0	111	158	206	103

21

22

23 The data in Table IV indicate that addition of TMOF to the phenolic resole resin
24 component in this case had some adverse affect on the core strength, particularly at the
25 1.4% level. It is noted that the presence of TMOF slightly increases the work time/strip
26 time of this no-bake binder. However, these adverse affects are not a problem from
27 commercial standpoint, and the advantages that the use of TMOF provides in terms of
28 increased heat stability outweighs these disadvantages.

⁴Weight percent based upon the weight of the phenolic resin component.

⁵Weight percent based upon the weight of the phenolic resin component.